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Production of Hydrogen-Containing Gas Using the Process of Steam-Plasma Gasification of Used Tires

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Abstract—The paper is devoted to treatment of used tires. The method of used tire gasification using steam plasma has been suggested. Studies of the composition of syngas depending on the process temperature and the steam-plasma flow rate have been performed. The method for increasing the hydrogen content in synthetic gas using the steam catalytic conversion of carbon monoxide contained in syngas in the presence of an absorber has been suggested. The results of the process mathematical simulation at different consumptions of steam and absorber are presented.

Keywords: tires, plasma gasification, steam catalytic conversion, hydrogen

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INTRODUCTION

At present, the global stock of used tires is estimated at 25 million tons [1]. Here, secondary use covers only ~23% of this amount. Since the remaining bulk is not utilized at all, due to the absence of an economically sound treatment method, the problem of the development of a novel technology for used tires treatment remains urgent. One of the methods of treatment of carbon-containing substances is their gasification, in which the combustible part, under the effect of thermal flows and blow agents, is transformed into syngas (a gas mixture consisting mainly of H_2 and CO), whereas the mineral part forms the ash residue.

Car tires have the following rough composition (wt %): rubber makes up 66.7%; textile cord, 15%; and metal cord, 18.3, corresponding to the element composition of C, which makes up 60.16%; H, 5.66%; O, 10.74%; N, 0.77%; Fe, 18.3%; and others, 4.37% [2, 3]. The lower heating value (LHV) of such tires approximately calculated on the ash-free state [4] is equal to 33.90 MJ/kg. Car tires have an element composition similar to that of black coal and, therefore, can be used as raw materials in the gasification process. The application of low-temperature plasma as an oxidizer during gasification is promising, since in this case, the end products' (CO and H_2) specific yield increases, the fraction of side products (CO_2, H_2O etc.) decreases, the rates of chemical reactions increase, and there emerges the possibility to control the process temperature and the plasma-forming gas flow rate within wide ranges [5–7]. The application of steam plasma enables one to obtain syngas, free of ballast gases [8–10]. Syngas can be applied for electric power generation [11] and in the processes of chemical synthesis [12]. Its application is also promising for the production of hydrogen-containing gas [13]. To increase the hydrogen content in syngas, it is feasible to perform the steam catalytic conversion of carbon monoxide. Implementing this process in two stages would provide high rates and the degree of the CO + H_2O mixture transformation into end products.

EXPERIMENTAL

Figure 1 shows the scheme of the process of producing hydrogen-containing gas from used car tires. The reactor-gasifier is fed with used car tires, and then they are gasified with steam plasma fed from the plasma torch. The ash residue is removed from the lower part of the reactor-gasifier. Wet syngas is quenched in a cooler (298 K): here, steam is condensed and separated from the gas flow. Dried syngas undergoes compression and catalytic steam conversion carried out in the presence of calcium oxide. As a result of the chemical interaction of the latter with carbon dioxide, calcium carbonate is formed, which results in shifting chemical equilibrium to the hydrogen side. Further, the flows of calcium carbonate and converted gas are separated. The conversion process is implemented in two stages at different temperatures. At the first stage, calcium oxide is fed in a stoichiometic quantity according to the reaction with carbon dioxide, and most of the carbon monoxide is con-

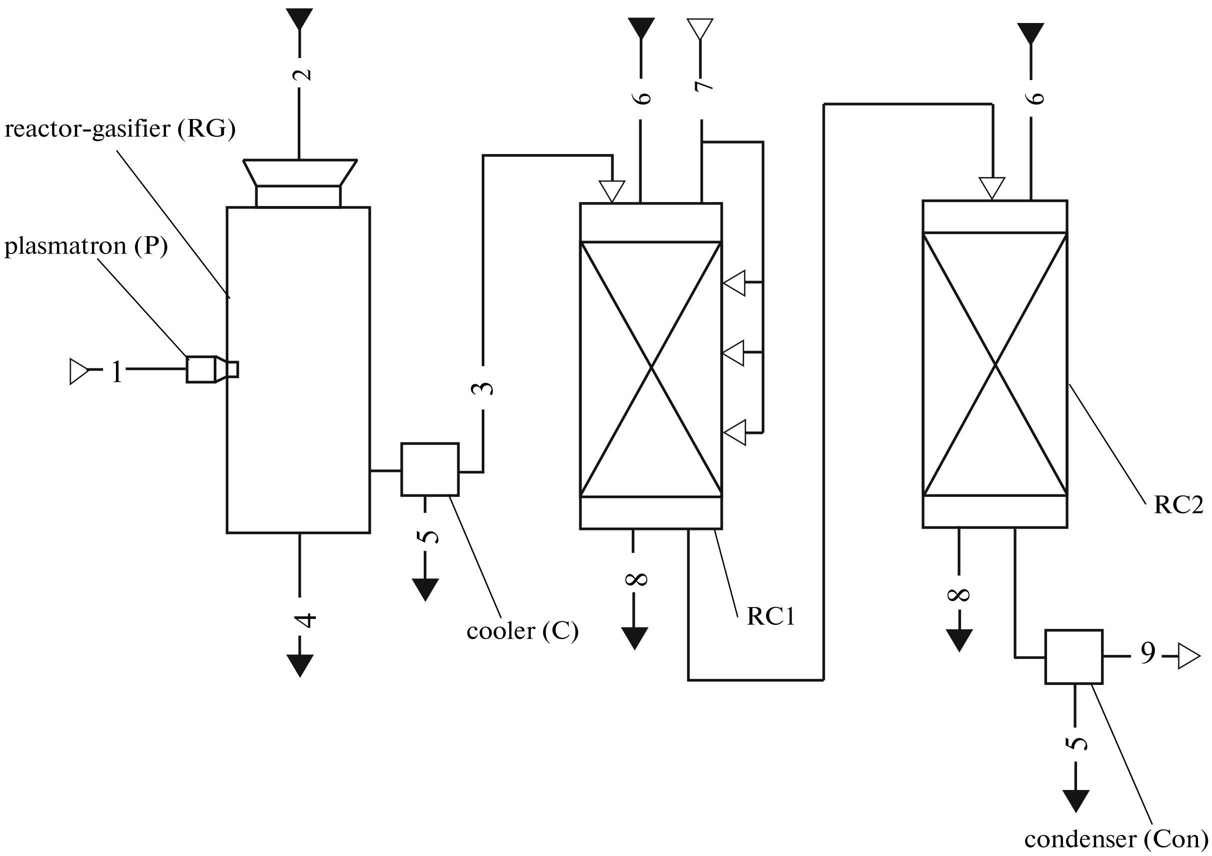

Fig. 1. Technological setup for the process of producing hydrogen-containing gas from used tires. 1. steam (creation of steam plasma); 2. used tires; 3. syngas; 4. ash; 5. condensate; 6. CaO; 7. steam; 8. $CaCO_3$; 9. hydrogen-containing gas.

verted: $CO + H_2O \longrightarrow CO_2 + H_2$, $CO_2 + CaO \longrightarrow CaCO_3$. At the second stage, an additional quantity of calcium oxide is added, and the conversion of the remaining quantity of carbon monoxide is performed.

To prevent the catalyst's deactivation by syngas nitrogen- and sulfur-containing components, one should use a catalyst containing cobalt and molybdenum deposited on a porous alumina substrate as active components.

The expended absorber undergoes regeneration. Hydrogen-containing gas is fed, upon conversion, into a condenser, in which it is separated from the condensate, and then goes to customers. The obtained hydrogen-containing gas can be used for the synthesis of ammonia and manufacturing of hydrochloric acid and ethanol.

Numerical Simulation of the Process

To simulate the process of steam-plasma gasification of car tires, the products composition was calculated under thermodynamic equilibrium conditions (using the software pack Chemical WorkBench ver. 3.5, Kinetic Technologies Ltd., http://www.kintech.ru). The dependence of changes in the composition of syngas on temperature at atmospheric pressure and the stoichiometric consumption of steam plasma was investigated: $C^{4+} + O^{2-} \longrightarrow CO$, $H^+ \longrightarrow 0.5H_2$. The stoichiometric consumption means that all the carbon and oxygen of the fuel and oxidizer are transformed into carbon monoxide, whereas hydrogen from the fuel is reduced until gaseous hydrogen and other elements of the fuel's organic part are oxidized. The obtained results are shown in Fig. 2.

As seen from Fig. 2, the formation of by-products occurs mainly at temperatures below 1200 K. In view of this, in order to produce syngas with the maximal contents of hydrogen and carbon monoxide, the process of plasma gasification of tires must be performed at temperatures of 1350 K and higher: in this case, the fraction of ballast gases will be close to zero.

Thereafter, the composition of the products of the process of plasma gasification of expended tires at 1350 K depending on the steam plasma consumption was calculated. The obtained results are shown in Fig. 3. As seen from Fig. 3, at the steam plasma consumptions of less than ~0.79 kg/kg graphite is formed, whereas with an increase of this consumption the contents of hydrogen and carbon monoxide decrease and the byproduct gases' content increases. The calcula-

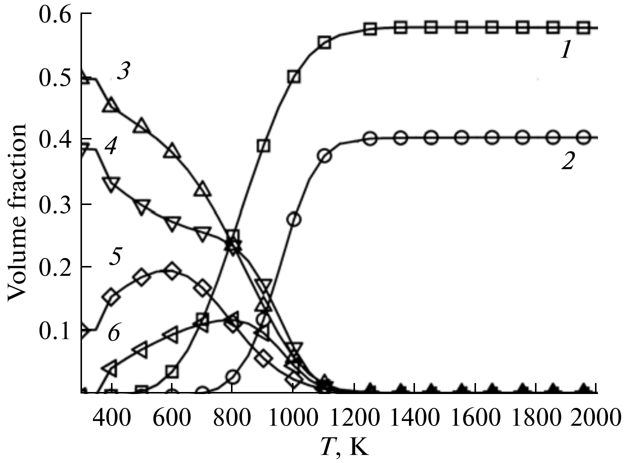

Fig. 2. Dependence of the yield of syngas components on temperature at stoichiometric consumption of steam and atmospheric pressure. *1.* H_2; *2.* CO; *3.* H_2O; *4.* C (graphite); *5.* CH_4; *6.* CO_2.

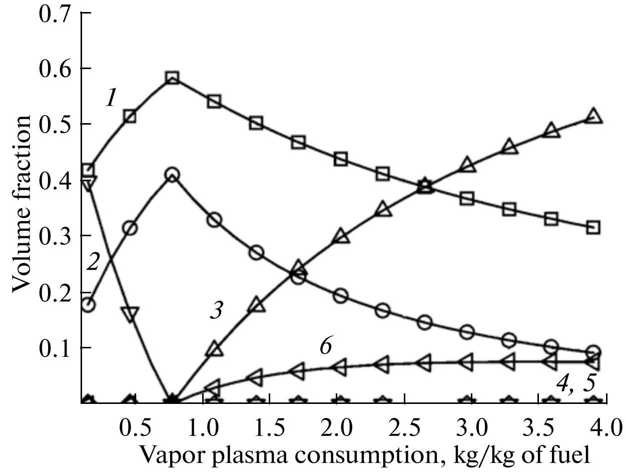

Fig. 3. Dependence of the syngas components' yield on the steam plasma consumption at 1350 K and atmospheric pressure. Markings as in Fig. 2.

tion was performed on 1 kg of used car tires, whose temperature at the gasifier inlet was 298.15 K. During the calculations, the following assumptions were applied: (1) the mineral part of the tires does not participate in the chemical process and does have a catalytic effect on it; (2) thermal losses are not taken into account (adiabatic process).

In order to estimate the main parameters of the process of hydrogen-containing gas production, the calculations were performed for the product of the steam conversion of carbon monoxide (contained in syngas) in the presence of calcium oxide. Here, the used calculated value of the power spent on the syngas compression was equal to ~0.18 kW h [14]. The parameters of calculations of the process of CO catalytic conversion are presented in Table 1. In order to accelerate the reactions, the process was carried out under elevated pressure, whereas the stages' temperature were selected in a way to ensure the total thermal effect of all the stages to approximate zero (except power consumptions on plasma gasification) near the optimal parameters.

In order to determine optimal process conditions, the calculations were performed for consumptions of 1–5 mol of water vapor per 1 mol of carbon of syngas ($CO + 0.5CH_4$) with an increment of 0.5 mol. The calculation of the first stage was carried out on the consumption of 1 mol of CaO per 1 mol of syngas ($CO + CO_2 + CH_4$); for the second stage, this was (1–3) mol per mol of carbon of syngas with an increment of 0.5 mol.

In the calculations, the heat of the formation of steam was taken into account, unlike power consumptions on the absorber and the catalyst's regeneration.

RESULTS AND DISCUSSION

The results demonstrated that at the stage of plasma gasification's total volume content of hydrogen plus carbon monoxide attains ~99.53% for steam flow rate ~0.79 kg per kg of tires and a temperature of 1350 K. The plasma heat content for this mode must be ~15.5 MJ/kg (13.0 MJ/kg without vapor formation heat) which is provided by the available state-of-the-art plasma torches [15].

The results of the mathematical simulation of the steam catalytic conversion process are shown in Figs. 4 and 5. As can be seen from the figures, along

Table 1. Initial data for calculating the catalytic steam conversion

Process characteristics		Conversion first stage	Conversion second stage
Temperature in reaction zone (K)		1023	823
Pressure in reactor (atm)		3	3
Temperature of raw materials feeding (K)	Syngas	298.15	–
	Hydrogen-containing gas	–	1023
	Steam	298.15	–
	Calcium oxide	298.15	298.15

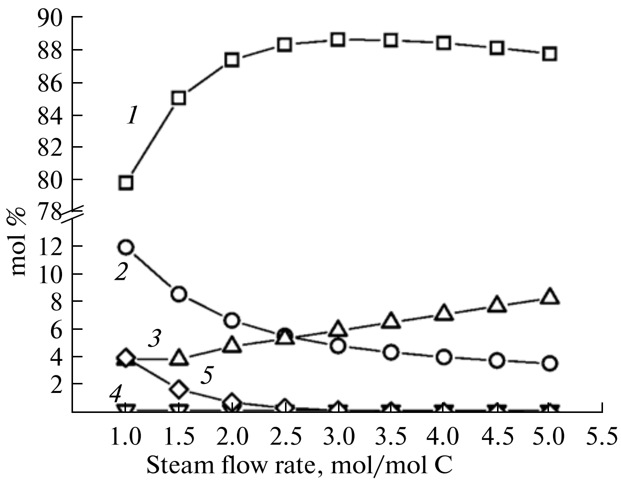

Fig. 4. Dependence of the hydrogen-containing gas components' yield on the steam flow rate at the first stage. *1.* H_2; *2.* CO; *3.* CO_2; *4.* N_2; *5.* CH_4.

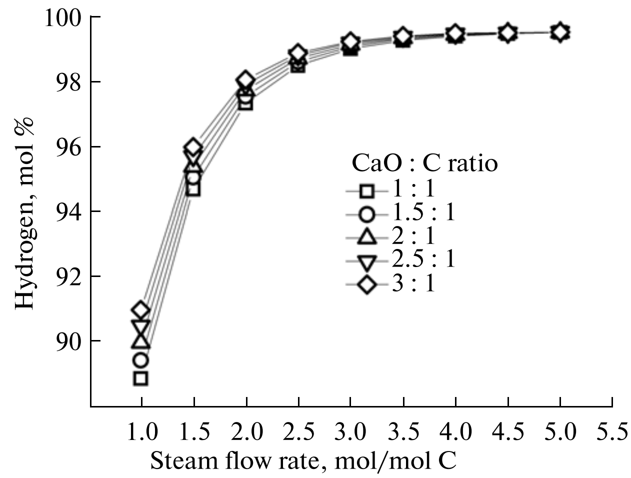

Fig. 5. Dependence of the hydrogen yield on the steam flow rate at the second stage.

with the increase of the steam flow rate at the first process stage (Fig. 4) the monoxide content decreases monotonously, whereas at the second stage (Fig. 5), the fraction of hydrogen increases. However, at the steam flow rate of 3.5 mol per mol of carbon and higher it barely changes.

The process of catalytic steam conversion of carbon monoxide is exothermal [16]. As can be seen from

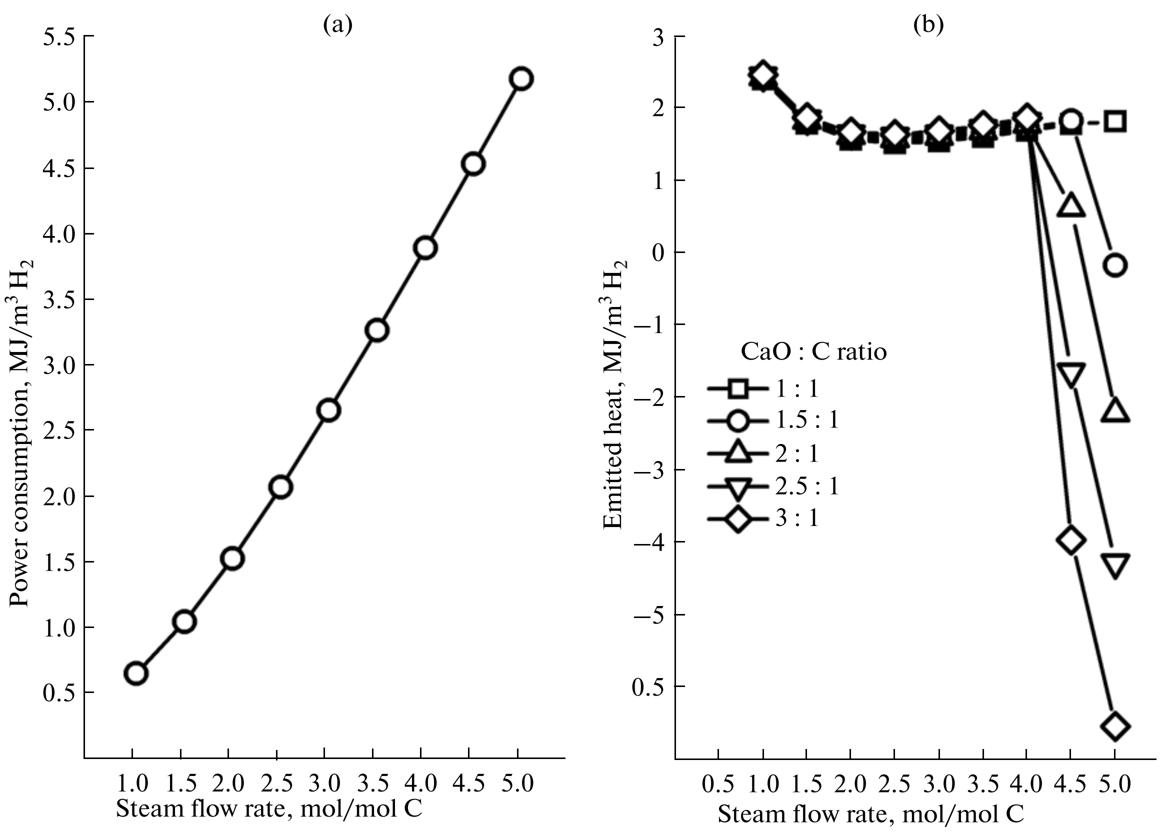

Fig. 6. Dependence of power consumption on the steam flow rate: (a) first stage; (b) second stage.

Table 2. Main specific parameters of the process of producing hydrogen-containing gas from used car tires

Process characteristics			Steam plasma gasification	CO steam conversion first stage	CO steam conversion second stage
Power consumption, kW h			3.39	3.09	–
Gas composition, vol %		H_2	58.54	88.45	99.47
		CO	40.99	7.16	0.01
		CO_2	0.17	4.08	0.06
		N_2	0.24	0.22	0.24
		CH_4	0.06	0.09	0.22
Material balance	Intake, kg	Car tires	1.00	–	–
		Syngas	–	1.56	–
		Hydrogen-containing gas	–	–	0.80
		Steam	0.79	3.60	2.80
		CaO	–	2.81	1.24
		Total	1.79	7.97	4.85
	Output, kg	Syngas	1.56	–	–
		Hydrogen-containing gas	–	0.80	0.26
		Steam	0.01	2.80	2.71
		Ash	0.22	–	–
		CaO	–	0.83	0.43
		$CaCO_3$	–	3.54	1.45
		Total	1.79	7.97	4.85
Syngas yield (m^3)			2.97	–	–
Hydrogen-containing gas yield (m^3)			–	3.19	2.87

Note: All calculations were made per kg of tires.

the calculation results, at the first stage, heat is spent only on heating syngas and steam. The second process stage occurs with a substantial heat emission. As seen from Fig. 6, at the first stage, with the increase of the steam flow rate power consumption increases. At the steam flow rate of 4.5 mol per mol of carbon and higher the value of heat emitted at the second stage decreases dramatically due to the formation of $Ca(OH)_2$. Changes in the calcium oxide consumption at the second stage of the process barely affect the hydrogen yield.

Table 2 shows the main parameters of the process of producing hydrogen-containing gas from used car tires.

CONCLUSIONS

As can be seen from the calculation results, 1 kg of used car tires, with the application of the process of steam-plasma gasification at 1350 K and steam flow rate of 0.79 kg per kg of tires, yields 3.0 m^3 (at 298 K) of syngas, consisting of 99.5% of hydrogen + carbon monoxide and having heat energy of 1.1 kW h. The catalytic conversion of the produced syngas at the steam flow rate of 4 mol per mol of carbon in the presence of a CaO absorber yields 2.9 m^3 of a gas containing ~99.5% of hydrogen. Here, the total heat effect of the conversion process is equal to 1.6 kW h and, taking into account the heat energy of the formed syngas, to 0.52 kW h. Thus, the power consumption on hydrogen production (without taking into account the consumption on catalyst recovery and absorber regeneration) will be 1.0 kW h of electric power per m^3 (298 K) of hydrogen and 0.43 kW h of heat energy per m^3 (298 K) of hydrogen.

REFERENCES

1. Moskvin, A.A. and Emel'yanova, M.N., Recycling of the Waste Automotive Tires in Russia: On the Way to Waste Production Technology, *Retsikling Otkhodov*, 2009, vol. 3, no. 21, pp. 2–5.
2. Lotosh, V.E., *Pererabotka otkhodov prirodopol'zovaniya* (Processing of Waste of the Nature Management), Yekaterinburg: Poligrafist, 2007 [in Russian].

3. Straka, P., Kriz, V., and Bucko, Z., Co-Gasification of Rubber with Brown Coal, *Acta Geodyn. Geomater.*, 2008, vol. 5, no. 151, pp. 329–334.

4. Reed, T.B. and Das, A., *Handbook of Biomass Downdraft Gasifier Engine Systems*, Golden (Colorado, United States): Solar Energy Research Institute, SERZISP-271-3022, 1988.

5. Bratsev, A.N., Popov, V.E., Shtengel', S.V., and Rutberg, A.Ph., Some Aspects of Development and Creation of Plasma Technology for Solid Waste Gasification, *High Temp. Mater. Processes* (New York), 2006, vol. 10, no. 4, pp. 549–556.

6. Bratsev, A.N., Kuznetsov, V.A., Popov, V.E., Rutberg, A.Ph., Ufimtsev, A.A., and Shtengel', S.V., Experimental Development of Methods on Plasma Gasification of Coal as the Basis for Creation of Liquid Fuel Technology, *High Temp. Mater. Processes* (New York), 2009, vol. 13, no. 2, pp. 147–154.

7. Brattsev, A.N., Kuznetsov, V.A., Popov, V.E., and Ufimtsev, A.A., Arc Gasification of Biomass: Example of Wood Residue, *High Temp.*, 2011, vol. 49, no. 2, pp. 244–248.

8. Popov, V.E., Bratsev, A.N., Kuznetsov, V.A., Shtengel', S.V., and Ufimtsev, A.A., Plasma Gasification of Waste as a Method of Energy Saving, *J. Phys.: Conf. Ser.*, 2011, vol. 275, no. 1, p. 012015.

9. Bratsev, A.N., Kuznetsov, V.A., Popov, V.E., Ufimtsev, A.A., and Shtengel', S.V., Estimation of Perceptivity of Steam-Plasma Methane Conversion, *High Temp. Mater. Processes* (New York), 2009, vol. 13, no. 2, pp. 241–246.

10. Rutberg, Ph.G., Bratsev, A.N., Kuznetsov, V.A., Popov, V.E., Ufimtsev, A.A., and Shtengel', S.V., On Efficiency of Plasma Gasification of Wood Residues, *Biomass Bioenergy,* 2011, vol. 35, no. 1, pp. 495–504.

11. Bratsev, A.N., Kumkova, I.I., Kuznetsov, V.A., Popov, V.E., Shtengel', S.V., and Ufimtsev, A.A., Air Plasma Gasification of RDF as a Prospective Method for Reduction of Carbon Dioxide Emission, *Inst. Phys. Conf. Ser.*, 2011, vol. 19, no. 1, p. 012004.

12. Rutberg, Ph.G., Kuznetsov, V.A., Bratsev, A.N., Popov, V.E., Shtengel', S.V., and Ufimtsev, A.A., Use of Carbon Dioxide in the Chemical Synthesis Technologies, Plasma Gasification, and Carbon Production, *Inst. Phys. Conf. Ser.,* 2011, vol. 19, no. 1, p. 012003.

13. Kuznetsov, V.A., Rutberg, F.G., Brattsev, A.N., Popov, V.E., Ufimtsev, A.A., Shtengel', S.V., Lerner, A.S., and Subbotin, D.I., Gasification of the Waste Automotive Tires by Air and Vapor Plasmas, *Ekotekhnol. Resursosberezhenie*, 2011, no. 2, pp. 46–50.

14. Floarea O. and Smigelschi O., *Calcule De Operath Si Utilaje Din Industria Chimica*, Bucharest: Editura Tehnica, 1966. Translated under the title *Raschety po protsessam i apparatam khimicheskoi tekhnologii,* Moscow: Khimiya, 1979 [in Romanian and in Russian].

15. Rutberg, Ph.G., Lukyanov, S.A., Kiselev, A.A., Kuschev, S.A., Nakonechny, Gh.V., Nikonov, A.V., Popov, S.D., Serba, E.O., Spodobin, V.A., and Surov, A.V., Investigation of Parameters of the Three Phase High-Voltage Alternating Current Plasma Generator with Power up to 100 kW Working on Steam, *J. Phys.: Conf. Ser.*, 2011, vol. 275, no. 1, p. 012006.

16. Baronskaya, N.A., Khasin, A.A., Smirnov, E.I., and Yur'eva, T.M., Variants of the Organization of a Controlled-Temperature-Profile Catalyst Bed in a Tubular Reactor for the Single-Step Water Gas Shift Reaction, *Theor. Found. Chem. Eng.,* 2009, vol. 43, no. 4, pp. 366–373.